

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **08-283970**
(43)Date of publication of application : **29.10.1996**

(51)Int.CI.

C23G 1/12

(21)Application number : **07-085793** (71)Applicant : **NIPPON STEEL CORP**

(22)Date of filing : **11.04.1995** (72)Inventor : **MATSUHASHI AKIRA
KIHIRA HIROSHI**

(54) METHOD FOR PICKLING TITANIUM THIN SHEET

(57)Abstract:

PURPOSE: To prevent the pickling contamination due to the deposition of colored TiO and Ti₂O₃ and to obtain a beautiful surface at the time of descaling an annealed titanium thin sheet by using a mixed soln. of the nitric acid and hydrofluoric acid having a specified concn. as a pickling soln. and conducting a series of operations such as water washing and drying after pickling without exposing the sheet to the air.

CONSTITUTION: A mixed soln. contg. 40-250g/l nitric acid and 20-50 hydrofluoric acid is used as the pickling soln., and a series of operations such as water washing and drying are conducted immediately after pickling. Further, hydrogen peroxide is preferably added by 50-200g/l to the pickling soln. More preferably, the pickled titanium thin sheet is dipped in 60-63% nitric acid kept at 40-60°C, washed with water and dried. By using such a highly oxidative pickling soln. and conducting the treatments after pickling, the titanium oxide formed on the surface is converted to colorless TiO₂, and the brownish pickling contamination is avoided.

LEGAL STATUS

[Date of request for examination] **18.10.1999**

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than abandonment
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application] **09.05.2001**

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's

decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

JPO and NCIPPI are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The acid-washing approach of the titanium sheet metal characterized by performing a series of actuation of rinsing and desiccation, without using the mixed solution of a nitric acid and fluoric acid as acid-washing liquid, and putting to air after acid washing in case the scale of titanium annealing sheet metal is removed.

[Claim 2] The acid-washing approach of the titanium sheet metal according to claim 1 characterized by using the mixed solution of the nitric acid which made concentration of a nitric acid 40 - 250 g/l (liter), and made concentration of fluoric acid 20 - 50 g/l, and fluoric acid as acid-washing liquid.

[Claim 3] The acid-washing approach of claim 1 characterized by using for the mixed solution of a nitric acid and fluoric acid the solution which added the hydrogen peroxide of further 50 - 200 g/l as acid-washing liquid, or titanium sheet metal given in two.

[Claim 4] The acid-washing after-treatment approach of the titanium sheet metal characterized by being immersed after acid-washing processing into 60 - 63% nitric-acid solution with a temperature of 40-60 degrees C by the acid-washing approach given in any of claims 1, 2, and 3 they are, and performing a series of actuation of rinsing and desiccation after that.

[Translation done.]

*** NOTICES ***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is an approach for obtaining the front face which does not have beautiful dirt after acid washing of titanium sheet metal about the descaling method of titanium annealing sheet metal, and is used in the manufacture field of titanium sheet metal.

[0002]

[Description of the Prior Art] Conventionally, generally acid washing is carried out, using the mixed solution (it being hereafter called a ** fluoric acid solution) of a nitric acid and fluoric acid as a descaling method of titanium annealing sheet metal, and the approach of subsequently rinsing and drying is adopted. However, when the case which it is put to air a process while once carrying out ejection rinsing of the titanium from a ** fluoric acid solution after descaling by the above-mentioned approach, and a brown corrosion product (it is called following acid washing dirt) produces on a titanium front face is often experienced by on-site operation and the titanium sheet metal product of a beautiful front face is manufactured stably, generating of this acid washing dirt poses a problem dramatically. "A beautiful front face" here shows the thing of a front face without brown acid-washing dirt.

[0003]

[Problem(s) to be Solved by the Invention] This invention cancels the acid-washing dirt on the front face of titanium after descaling of titanium annealing sheet metal, and relates to the acid-washing approach for offering stably practically the titanium sheet metal of the beautiful front face which does not pose a problem, and the acid-washing after-treatment approach.

[0004]

[Means for Solving the Problem] this invention persons became clear [the following points], as a result of examining various pickling and the acid-washing after-treatment methods for obtaining the beautiful front face which was markedly alike and was excellent as compared with beautiful [of the front face obtained from an above-mentioned viewpoint by pickling of the titanium annealing sheet metal by the conventional ** fluoric acid solution].

[0005] First, in order to clarify an acid-washing dirt factor, image-analysis equipment considered the relation of the time amount (it is only hereafter called the neglect time amount) and acid-washing dirt which left titanium annealing sheet metal in air until it rinses after acid washing in the ** fluoric acid solution containing the various nitric acids and the fluoric acid of concentration. Consequently, as for acid-washing dirt, nitric-acid concentration is high and fluoric acid concentration made low clearly the fundamental condition range which traces that it is so few that neglect time amount is moreover short etc., and does not produce acid-washing dirt.

[0006] Subsequently, when actual condition analysis of the acid-washing dirt matter of a

titanium sheet metal front face was performed, the oxide (TiO and Ti_2O_3) which consists of the + divalent and the + trivalent of titanium existed in the front face on which acid-washing dirt exists, and the oxide of + tetravalence of titanium (TiO_2) was detected in the titanium front face without acid-washing dirt. From this, the cause of acid-washing dirt showed clearly that it originates in the mixture of a + divalent and + trivalent colored titanic-acid ghost having adhered to the titanium front face.

[0007] The basic principle that what is necessary is just to change the titanic-acid ghost generated on a front face using the acid-washing liquid or acid-washing after-treatment liquid of a high oxidizing quality to avoid acid-washing dirt from a further above-mentioned result to the higher order colorless oxide of + tetravalence was traced.

[0008] In case this invention removes the scale of (1) titanium annealing sheet metal based on the above-mentioned knowledge It is the acid-washing approach of titanium sheet metal of performing a series of actuation of rinsing and desiccation, without putting to air after acid washing, using the mixed solution of a nitric acid and fluoric acid as acid-washing liquid. (2) Concentration of a nitric acid is made into 40 - 250 g/l (liter) in the acid-washing approach of the above-mentioned (1) term. The mixed solution of the nitric acid which made concentration of fluoric acid 20 - 50 g/l, and fluoric acid is used as acid-washing liquid. The acid-washing approach of titanium sheet metal of performing a series of actuation of rinsing and desiccation, without putting to air after acid washing, And the acid-washing approach of titanium sheet metal of performing a series of actuation of rinsing and desiccation after acid washing, using the solution which added the hydrogen peroxide of further 50 - 200 g/l to the mixed solution of a nitric acid and fluoric acid in which acid-washing approach of the (3) above-mentioned (1) term and (2) terms as acid-washing liquid. Furthermore, it is immersed after acid-washing processing into 60 - 63% nitric-acid solution with a temperature of 40-60 degrees C by which acid-washing approach of the (4) above-mentioned (1) term, (2) terms, and (3) terms, and let after that the acid-washing after-treatment approach of titanium sheet metal of performing a series of actuation of rinsing and desiccation be a summary.

[0009] In addition, since it is possible to remove acid-washing dirt by maintaining a high oxidizing quality theoretically, acid-washing dirt is removable, although invention of the above-mentioned (4) term is an acid-washing after-treatment method immersed in titanium sheet metal into 60 - 63% nitric-acid solution with anode electrolysis in a low concentration nitric acid.

[0010] The reason for definition of the acid-washing terms and conditions of this invention is explained below.

Nitric-acid concentration in a ** fluoric-acid solution: 40 - 250 g/l (liter)

A nitric acid is the basic acid-washing liquid of this pickling, and is also an oxidizer. + In order to oxidize to + tetravalence in most titanium ion which dissolved with divalent, the concentration of at least 40 or more g/l was required, and although this oxidizing power went up, when the nitric acid was made to contain exceeding 250 g/l, since the solution temperature of acid washing liquid rose and a great effort and expense started control by the acid washing reaction, the upper limit was made into 250 g/l, so that concentration became high.

[0011] Fluoric-acid concentration of a ** fluoric-acid solution: It is basic acid-washing liquid like a nitric acid, and although 20-50g [l.] fluoric acid has the strong work which accelerates the dissolution rate of titanium, on the other hand, it is also an acid with strong reducibility. In order to secure the amount of dissolutions of titanium, the minimum and the concentration of 20 or more g/l are required. The amount of dissolutions increases so that concentration becomes high, but when fluoric acid is made to contain exceeding 50 g/l, the titanium ion which dissolved since

reducibility became strong stops being able to change to high order ion easily, and acid-washing dirt becomes large as a result.

[0012] Hydrogen-peroxide concentration: A 50 - 200 g/l hydrogen peroxide has strong work of an oxidizer like a nitric acid. Therefore, if a hydrogen peroxide is added in a ** fluoric acid solution, acid-washing dirt will decrease in number further. Avoiding generation of heat of the acid-washing liquid by the acid-washing reaction, in order to decrease acid-washing dirt, at least 50 g/l is required. Even if it adds exceeding 200 g/l, effectiveness is saturated and is not economical.

[0013] nitric-acid concentration [of acid-washing after treatment]: -- 60 - 63%, and temperature: -- it uses for the processing for removing the acid-washing dirt of the titanium material which 40-60 degrees C of acid-washing dirt already produced. The nitric acid of this concentration is usually called concentrated nitric acid, and is the threshold value concentration in marketing. Although effectiveness becomes large, it requires great time amount for effectiveness showing up below 40 degrees C, and is not so productive as temperature is high. Moreover, it is [evaporation of the water from liquid and evaporation of a nitric acid become great, and] hard to control by temperature of 60 degrees C or more and is not practical.

[0014]

[Example] Based on an example, this invention is explained below. What carried out vacuum annealing of the cold-rolled plate (0.8mm of board thickness) of one sort of commercially pure titanium to the test specimen was extracted, and acid-washing processing was performed in the ** fluoric acid solution of various concentration. after acid-washing processing boils various neglect time amount to ejection and rinsing, changed the titanium annealing plate, rinsed it and carried out hot air drying from acid-washing liquid after a titanium annealing plate is immersed for 80 seconds into the acid-washing liquid which kept it warm at 45 degrees C, it asked for the rate of acid-washing dirt area with image-analysis equipment.

[0015] The effect of the neglect time amount before ***** nitric-acid concentration and rinsing is shown in the rate of acid-washing dirt area at drawing 1. Moreover, a reference drawing is submitted independently and the situation of acid-washing dirt is shown. the front face of the titanium to each neglect time amount before rinsing at the time of a reference drawing fixing the fluoric acid concentration in a ** fluoric acid solution to 45 g/l, and changing nitric-acid concentration to 0 - 100 g/l -- it is the photograph in which description was shown and the part which is visible to the brown on a titanium front face in this drawing is acid-washing dirt. Although the rate of acid-washing dirt area is 0 also in which nitric-acid concentration in drawing 1 in the case where the neglect time amount before rinsing is 0 second, the rate of acid-washing dirt area is increasing by the low concentration nitric-acid side as the neglect time amount before rinsing becomes long. When the rate of acid-washing dirt area was 0.1% or less substantially, since acid-washing dirt had not been recognized, as it was shown below, it judged under each acid-washing condition and after-treatment conditions.

O : the rate of acid-washing dirt area is 0.1% or less. With no acid-washing dirt x: The rate of acid-washing dirt area is larger than 0.1%. Those with acid-washing dirt [0016] The result of having evaluated acid-washing dirt in accordance with the above-mentioned criterion (it having been neglect time amount 6 seconds before rinsing.) was shown in a table 1. This shows that the sheet metal which has the beautiful titanium front face which does not have acid-washing dirt in acid washing of titanium annealing sheet metal by the approach of this invention is obtained.

[0017]

[A table 1]

[0018]

[Effect of the Invention] By this invention, the very beautiful titanium sheet metal which does not have acid-washing dirt in acid washing of titanium annealing sheet metal can manufacture now stably.

[Translation done.]

* NOTICES *

JPO and NCIPPI are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The fluoric acid concentration in a ** fluoric acid solution is fixed to 45 g/l, and the rate of acid-washing dirt area of the front face of the titanium to each neglect time amount before rinsing at the time of changing nitric-acid concentration to 0 - 100 g/l is plotted to nitric-acid concentration.

[Translation done.]

* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

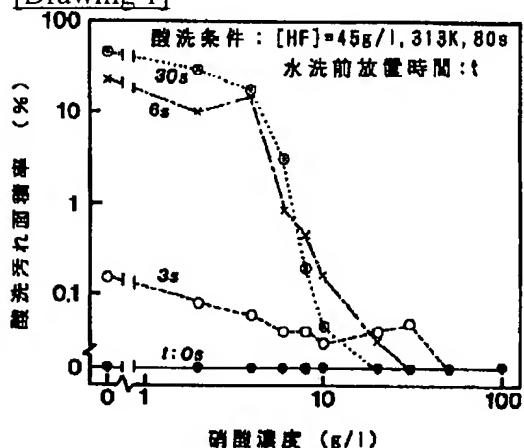
1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]